ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 120 (1999) 11–14

Journal of Photochemistry and Photobiology A:Chemistry

Flash-photolysis studies of *trans*-[Cr cyclam$(CN)_2$]ClO_4 (cyclam = 1,4,7,11-tetraaza-cyclotetradecane) complex Part 2 Unexpected self-quenching and its connection to the apparent activation energies of the complex

László Vincze*, Flórián Sándor, Judit Pém, Gyöngyi Bosnyák

Department of General and Inorganic Chemistry, University of Veszprém, 8201 P.O. Box 158, Veszprém, Hungary

Received 14 July 1998; received in revised form 28 July 1998; accepted 21 September 1998

Abstract

The luminescence lifetime (τ_{lum}) of the title complex **I** was determined in eight solvents. We found that in spite of former assumptions, τ_{lum} of **I** depends on the concentration of the complex. We determined the self-quenching- and Stern–Volmer constants (K_{SV}), and the relative values of luminescence quantum yields in eight solvents. There was no measurable self-quenching in 1,2-ethane-diol and *N,N*-dimethyl-formamide, dynamic self-quenching was found (the concentration dependence of τ_{lum} and ϕ_{lum} was the same) in *N,N*-dimethyl-acetamide, dimethylsulfoxide, water, propylene-carbonate, pyridine. In acetonitrile we found both dynamic and static self-quenching based on the different concentration dependence of τ_{lum} and ϕ_{lum} of **I**; K_{SV} and the association constant of **I** in acetonitrile were computed. The apparent activation energies were also studied, they decreased when the self-quenching became faster. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cr-cyclam; Luminescence lifetime; Self-quenching; Stern–Volmer constants; Activation energy (apparent)

1. Introduction

The luminescence lifetime of the *trans*-[Cr(cyclam)$(CN)_2$]ClO_4 complex has been measured by several authors [1–5] so far, but the concentration dependence of the luminescence lifetime was either not studied [3–5] or no significant concentration dependence was found [1,2]. In the case of the similar *trans*-[Cr(cyclam)$(NH_3)_2$]$(OTS)_3$ complex, our experiments [6] excluded the possibility of concentration dependence of the luminescence lifetime higher than the experimental errors. So it was a surprise when in aqueous solutions we found that the luminescence lifetime of the *trans*-[Cr(cyclam)$(CN)_2$]ClO_4 complex slightly but certainly depended on the concentration of the complex. Furthermore, the temperature-dependence of luminescence lifetime and the apparent activation energies of the *trans*-[Cr-cyclam$(CN)_2$]ClO_4 complex were not tudied either, so our objective was to study the dependence of luminescence lifetimes on solvent, concentration and temperature.

2. Experimental

2.1. Instruments and computations

The UV–Vis spectra were recorded by M-40 UV–Vis spectrophotometer (Carl Zeiss, Jena).

The luminescence spectra were determined both with an LS50 luminescence spectrophotometer (Perkin-Elmer), and also based on the transients generated by flashes of a Brilliant laser (Quantel). The transients were recorded between 600 and 800 nm. The output of the laser was followed, and its change was less then ±5%.

The luminescence lifetime of the complex was studied by the laser flash photolysis instrument assembled at our Department. The instrument includes the Brilliant laser, an Applied Photophysics kinetic spectrometer, PM 3320A Phillips data-storing oscilloscope, and an IBM compatible PC for instrument control and information storage. The normal emission wavelength of the Brilliant laser is 1064 nm and that wavelength was modified to 355 nm with a frequency-tripler system. The characteristic data of pulses are: 1.6×10^{17} photons are emitted at 355 nm (90 mJ),

---

*Corresponding author.

1010-6030/99/$ – see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(98)00410-9

fwhm is 4.2 ns. The software which controls the instrument was developed at our Department. Further details are described elsewhere [5].

All measurements (UV–Vis and luminescence spectra, flash photolysis transients) were evaluated with Excel 5.0.

Luminescence lifetimes were computed from transients recorded at about 715 nm where the highest peak of the luminescence spectra was. The timespans of transients used were at least three times longer than the lifetime concerned. Each lifetime was the average of 3–4 measurements, and each measurement included the evaluation of 8–20 transients.

2.2. Chemicals

$CrCl_3.3THF$ and cyclam were purchased from Aldrich, their purities were 99% and 98%, respectively. Millipore Q water and Aldrich solvents of HPLC quality [dimethylsulfoxide (DMSO),*N,N*-dimethyl-formamide (DMF), *N,N*-dimethyl-acetamide (DMA), pyridine, acetonitrile, 1,2-ethanediol and propylene-carbonate] were used. Chemicals were used without further purification.

2.3. Preparation of trans-[Cr-cyclam(CN)$_2$]ClO$_4$ and samples

Trans-[Cr-cyclam$(CN)_2$]ClO_4 was prepared according to the literature [4,5]. Solutions were freshly prepared, their concentrations were 1×10^{-4}–2×10^{-3} M, depending on solubilities. Samples were not deoxygenated, since the presence or absence of oxygen had no effect on the τ_{lum} or on the spectra of the complex [5,6].

3. Results and Discussion

3.1. Concentration dependence of luminescence lifetimes

The luminescence lifetimes of the complex taken in different solvents and calculated to zero complex concentration are summarized in Table 1. The luminescence lifetimes of the complex depended on the concentration in the majority of the applied solvents, only in DMF and 1,2-ethane-diol was the concentration dependence unmeasurable. The luminescence quantum yields were about the same (around 10^{-3} according to Serpone [7]), depending only slightly on the concentration of the complex, but in acetonitrile the luminescence quantum yield decreased quickly when the concentration increased (Table 2). The self-quenching rate constants and the Stern–Volmer constants are also collected in Table 1. It can be seen that in five solvents the Stern–Volmer constants are around 10^2 M^{-1}, but in acetonitrile the Stern–Volmer constant was 90 times higher than in the other solvents.

In water, DMA, DMSO, propylene-carbonate and pyridine we assumed dynamic quenching based on the facts, that the τ_{lum} and the luminescence quantum yields changed parallelly (Fig. 1). In case of dynamic quenching, the excited complex can lose its excess energy by colliding with a ground state complex. Ground state complex is abundantly available, because in the irradiated volume only 4% of the complexes will be excited, 96% of them remain in the ground state. It can be shown by the following short calculations: the number of excited (N_{exc}) and ground state (N_{ground}) complexes can be given by Eq. (1):

Table 2
Relative luminescence quantum-yields (related to luminescence quantum-yield of water) of the complex in several solvents ($t = 20°C$)

No	Solvent	Range of c (mM)	$\phi_{lum,\ rel}$
1	1,2-ethane-diol	0.05–0.6	1.1
2	DMF	0.3–2.0	0.8
3	DMA	0.1–0.5	1.1–1.2
4	DMSO	0.05–1.0	1.0–1.1
5	Water	0.1–2.0	1.0–1.2
6	Propylene-carbonate	0.1–1.0	1.0–1.1
7	Pyridine	0.1–0.3	0.9–1.0
8	Acetonitrile	0.05	0.52
9	Acetonitrile	0.1	0.42
10	Acetonitrile	0.2	0.27
11	Acetonitrile	0.3	0.21
12	Acetonitrile	0.6	0.13
13	Acetonitrile	1.0	0.06

Table 1
Self-quenching and Stern–Volmer constants, and apparent activation energies of the *trans*-[Cr(cyclam)$(CN)_2$]ClO_4 complex. Luminescence lifetimes were calculated to zero concentration of the complex ($t = 20°C$)

No	Solvent	τ_0 (μs)	k_Q (10^6 M^{-1} s^{-1})	K_{SV} (M^{-1})	$E_{A(app)}$ (kJ mol^{-1})
1	1,2-ethane-diol	175	<0.1	<0.1	32.8
2	DMF	34.1	<0.1	<0.1	29.3
3	DMA	59.4	1.02	50	25.8
4	DMSO	43.6	0.55	96	25.3
5	Water	339	0.25	86	10.4
6	Propylene-carbonate	340	0.44	151	11
7	Pyridine	10.0	17.3	180	8.1
8	Acetonitrile	120	59.5	9.0×10^3	7.6

Note: We tried to prepare solutions of the complex by using solvents methanol, ethanol, propanols, buthanols, propylamine, buthylamines, 2-cyano-pyridine, 2-methoxy-pyridine, pyrimidine, but the complex was not soluble in them.

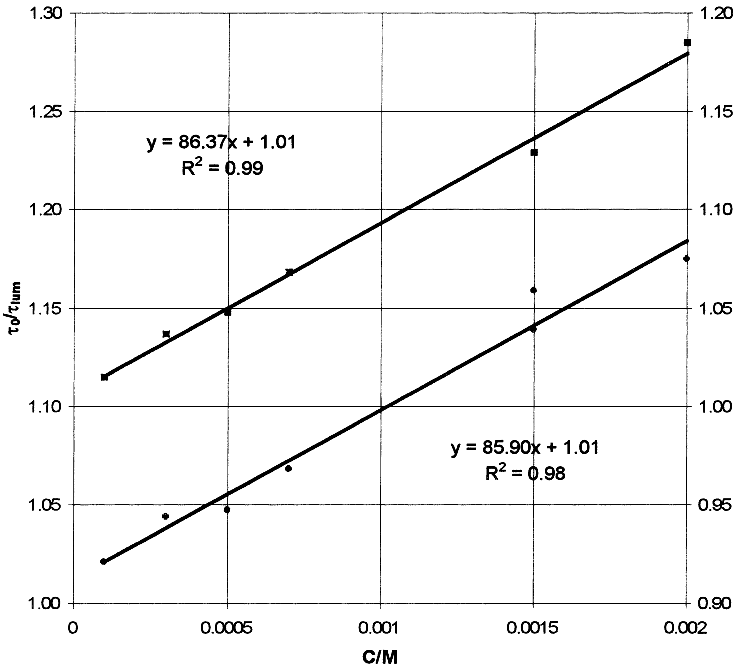

Fig. 1. Stern–Volmer plot for τ_0/τ (•) and ϕ_0/ϕ (■) of the complex in water.

$$\frac{N_{\rm exc}}{N_{\rm ground}} = \frac{N_{\rm exc}}{N_0 - N_{\rm exc}} \tag{1}$$

where $N_{\rm exc} \cong N_{\rm pulse}(1-10^{-\varepsilon cd}) = N_{\rm pulse} * 2.3\varepsilon cd$, and $N_0 = VcN_{\rm A}$, so

$$\alpha = \frac{2.3N_{\rm pulse}\varepsilon cd}{VcN_{\rm A} - 2.3N_{\rm pulse}\varepsilon cd} \tag{2}$$

$N_{\rm pulse}$=1.6×10^{17} photons, $\varepsilon_{355} = 24\ {\rm M}^{-1}\ {\rm cm}^{-1}$, d = 1 cm, the cross-section of the laser beam is 0.385 cm^2, so the irradiated volume (V) is 3.85×10^{-4} dm^3. With these data, α is approximately equal to 4%.

On the other hand, in acetonitrile both dynamic and static quenching can be assumed, since the concentration dependence of $\tau_{\rm lum}$ and the luminescence quantum yield was different (Fig. 2). The static self-quenching means dimer formation ($\mathbf{I}_2$), therefore on the abscissa of Fig. 2 the free complex concentration is plotted, not its total analytical concentration . The reciprocal $\tau_{\rm lum}$ is a linear function of the concentration, showing the effect of the dynamic quenching. The slope gives the Stern–Volmer constant,

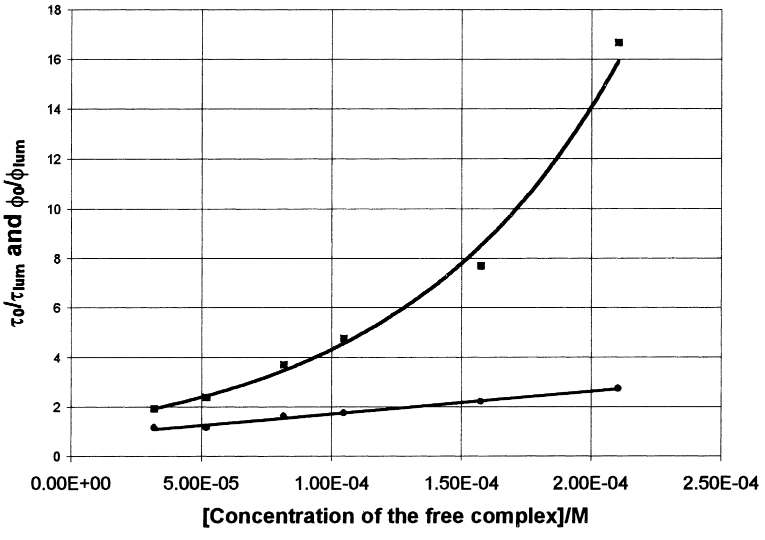

Fig. 2. Stern–Volmer plot for τ_0/τ (•) and ϕ_0/ϕ (■) of the complex in acetonitrile.

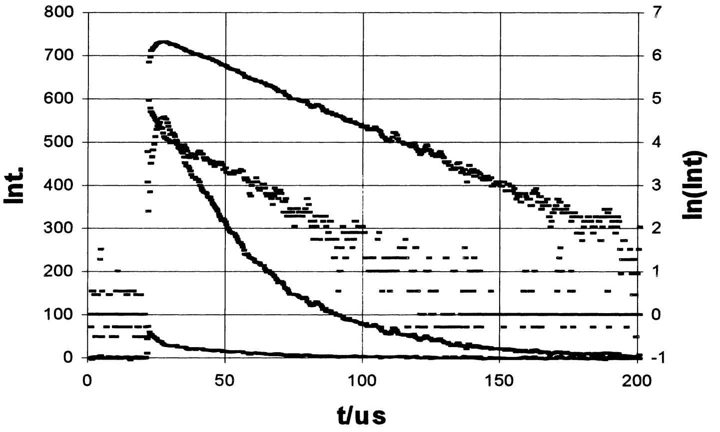

Fig. 3. Comparison of transients̀ dependence on pulse energy. Upper transient and linearized data: 90 mJ; lower transient and linearized data: 5 mJ.

which is equal to 9.0×10^3 M^{-1} in acetonitrile. The reciprocal luminescence quantum yield is not a linear function of the concentration, and increases faster than the reciprocal τ_{lum}, showing clearly the presence of the static quenching as well. In this case ϕ_0/ϕ_{lum} can be written [8] as:

$$\frac{\phi_0}{\phi_{lum}} = (1 + K_m[\mathbf{I}]) \times (1 + K_{SV}[\mathbf{I}]) \qquad (3)$$

where [**I**] is the free complex concentration; K_m is the association constant, multiplied by $\varepsilon_{I_2}/\varepsilon_I$ [8]; K_{SV} is the Stern–Volmer constant, calculated from ϕ_{lum}.

The optimum values of K_m and K_{SV} were 8.9×10^3 M^{-1} and 9.0×10^3 M^{-1}, respectively. The values of K_{SV} calculated from τ_{lum} and ϕ_{lum} are equal within the estimated experimental error.

We expected to find similar results in pyridine as well because of the lone pair on the pyridine-nitrogen, but according to the experiences the acetonitrile can have a much stronger mutual effect with the *trans*-[Cr(cyclam)-$(CN)_2$]ClO_4 than the pyridine has.

We studied the effect of pulse energy on the error of luminescence lifetimes and on the quality of luminescence transients. The pulses of 5 mJ energy induced such a weak luminescence that the relative error of computed lifetime was 7–10%, whereas at pulses of 90 mJ energy the relative error of computed lifetime was only 1–2% and the transients became well evaluable. These points are demonstrated in Fig. 3. The results suggest that the luminescence studies of the *trans*-[Cr(cyclam)$(CN)_2$]ClO_4 complex require at least 20–40 mJ energy per pulse.

3.2. Temperature dependence of luminescence lifetimes

We determined the temperature dependence of luminescence lifetime between 293–353 K in eight solvents. The results are summarized in Table 1. The values of apparent activation energies are not too high, they are about half of those of *trans*-[Cr cyclam$(NH_3)_2$]$(OTS)_3$ complex [6]. In 1,2-ethanediol the apparent activation energy is higher than the average and it can be interpreted by the viscosity decrease of 1,2-ethanediol with increasing temperature.

As far as the apparent activation energies in other solvents are concerned, they are connected to the self-quenching constant (k_Q). Two-third of the data are in a relatively close cluster but there are deviating points showing the following tendency: to low k_Q high apparent activation energies, and to high k_Q rather low (7.6–8.1 kJ mol^{-1}) apparent activation energies belong. It can be assumed that in case of strong quenching the effect of increasing temperature on τ_{lum} cannot be so significant than otherwise, when the quenching effect is weak.

Acknowledgements

The financial support of the Hungarian Academy of Sciences (T017348) is gratefully acknowledged.

References

[1] N.A.P. Kane-Maguire, W.S. Crippen, P.K. Miller, Inorg. Chem. 22 (1983) 696.
[2] D.G. Speece, M.S. Thesis, Furmann University, 1986.
[3] R.B. Lessard, M.J. Heeg, J.F. Endicott, Inorg. Chem. 31 (1992) 3091.
[4] N.A.P. Kane-Maguire, J.A. Bennett, P.K. Miller, Inorg. Chim. Acta 76 (1983) L123.
[5] Gy. Bosnyák, L. Vincze, J. Photochem. Photobiol. A 111 (1997) 23.
[6] L. Vincze, D.A. Friesen, S.P. Mezyk, W.L. Waltz, Inorg. Chem. 31 (1992) 4950.
[7] N. Serpone, M.A. Jamieson, R. Shiram, Z. Hoffman, Inorg. Chem. 20 (1981) 3983.
[8] A. Horváth, Inorganic Photochemistry, University of Veszprém Press, Veszprém, 1998.